I. QUINOXALINE FORMATION AND THE ORTHO EFFECT
II. HINDRANCE AT THE BETA CARBON ATOM

BY

QUENTIN FRANCIS SOPER

B. Chem., University of Minnesota, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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I. QUINOXALINE FORMATION AND THE ORTHO EFFECT

Introduction

The introduction of nitro groups on the aromatic ring of certain hindered molecules has been shown to relieve the obstruction to reactions that is usually associated with the ortho effect. The inability of mesityl phenyl diketone[1] and mesitylglyoxal[2] to form quinoxalines whereas 2-methoxy-4,6-dimethylphenylglyoxal[3] and 3,5-dinitromesitylglyoxal[3] easily produced the expected diazines, suggested immediately the use of the quinoxaline reaction as a device for the further study of the ortho effect and the influence of the other substituents on the "hindrance" phenomenon.

Experimental and Discussion

The diketones studied in this research usually were prepared as follows: $ArCH_2COCl \rightarrow ArCH_2COAr' \rightarrow ArCOCOAr'$. The glyoxals were obtained by the selenium dioxide oxidation of the corresponding acetophenones.

In the case of mesityl glyoxals it was found necessary to introduce two groups into the hindered molecule before quinoxaline formation was permitted. Thus, the action of *o*-phenylenediamine on 3-nitromesitylglyoxal and 3-bromomesitylglyoxal produced the corresponding Schiff bases whereas 3-bromo-5-nitromesitylglyoxal gave a quinoxaline.

Although 3,5-dinitromesityl 3-nitrophenyl diketone, which was obtained by the nitration of mesityl phenyl diketone, easily formed a quinoxaline, it was unnecessary for more than one nitro group to be present for the reaction to occur. The truth of this statement was demonstrated by the successful condensation of 3-nitromesityl phenyl diketone with the diamine. The formation of a quinoxaline from 3,5-dibromomesityl phenyl diketone,[4] 3-nitromesityl 4-nitrophenyl diketone and the preceding results indicated that hydrogen bonding of the *ortho* methyl group with the nitro groups (or bromine atoms) was relieving the hindrance.

This hypothesis, however, could not explain the results of later experiments. It was found that mesityl 4-nitrophenyl diketone, mesityl 3-nitrophenyl diketone and 4-bromophenyl mesityl diketone all yielded quinoxalines very easily. The similarity of the reaction of the compounds of type ArCOCO-C_6H_4X-4 and those of the vinylog, ArCOCOX, is of interest and may aid in explaining the observed phenomena.

The inability of tipylglyoxal, 3,5-dinitrotipylgloxal, 3,5-dinitrotipyl 3-nitrophenyl diketone, tetranitromesitil and 4,4'-dimethoxy-2,6-xylil to form quinoxalines reveals that the introduction of groups has no appreciable effect on the more highly hindered 1,2-dicarbonyl compounds.

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II. HINDRANCE AT THE BETA CARBON ATOM

Introduction

The evidence which is now available, indicates that the stability of non-chelated enols depends in a greater degree on space exigency at the *beta* than at the *alpha* carbon atom.[1,2] This investigation deals with the accumulation of evidence in further support of this theory. For this purpose various mixed enols from combinations of phenyl and tipyl radicals were prepared.

Experimental and Discussion

Oxidation of benzyl tipyl ketone with selenium dioxide gave an 85 per cent yield of phenyl tipyl diketone (I). This diketone was reduced catalytically to give 1-phenyl-2-tipyl-ethylene glycol (II), which could be identified only in solution. Attempts to isolate this enediol (II) yielded only 2,4,6-triisopropylbenzoin (III) or the diketone (I). The formation of the benzoin (III) to the exclusion of the 2', 4', 6'-triisopropylbenzoin, is a strong indication that it is the hindrance at the *beta* carbon atom which is largely responsible for the stabilization of these enol types.

The reduction of the diketone (I) or the benzoin (III) with hydriodic acid gave an excellent yield of 2', 4', 6'-triisopropyldesoxybenzoin, and this product condensed with formaldehyde to yield phenyl ∝-tipylvinyl ketone. The catalytic reduction of this ketone gave 1-phenyl-2-tipyl-1-propen-1-ol (IV), an enol which could be isolated although it rapidly absorbed oxygen from the air to give a stable peroxide. In this case the hindering radical, the tipyl group, is *beta* to the hydroxyl group. The keto form was obtained by distillation of the peroxide.

Attempts to prepare the isomeric enol, 2-phenyl-1-tipyl-1-propen-1-ol (V) met with failure. The synthesis of the enol by the reduction of ∝-phenylvinyl tipyl ketone failed due to the inability to prepare the latter ketone. ∝-Phenylethyl tipyl ketone, which resulted from the condensation of hydratropic acid chloride with tipylene, would not enolize under the influence of sodium ethoxide or methylmagnesium iodide, the usual enolizing agents. The inability to isolate this enol (V), in which the hindering tipyl group is *alpha* to the hydroxyl radical, further substantiates the theory of *beta* hindrance.

2-Phenyl-2-tipylvinyl alcohol could not be prepared by the dehydration of 1-phenyl-2-tipylethylene glycol (VI) although the corresponding 2-mesityl-2-phenylvinyl alcohol has been obtained in this manner[2] and has been shown to be stable. The glycol (VI) was obtained by the high-pressure, catalytic hydrogenation of the diketone (I). A non-crystalline mixture of products was obtained from dehydration reactions.

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Vita

The author was born in Buhl, Minnesota on December 3, 1919. He attended the elementary school of Calumet, Minnesota and graduated from Greenway High School, Coleraine, Minnesota in June, 1936. He entered Itasca Junior College of that city in the fall and was granted the degree of Associate of Arts in June, 1938. That September he matriculated at the University of Minnesota, from which he received the Bachelor of Chemistry degree in June, 1940. In the fall of the same year he entered the Graduate School of the University of Illinois. He was a teaching assistant from 1940 to 1942 and held a University Fellowship during the year 1942-1943.

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